

# Comment on “Density functional theory study of some structural and energetic properties of small lithium clusters” [J. Chem. Phys. 105, 9933 (1996)]

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The experimentally determined size-evolutionary patterns (SEPs) of simple metal clusters pertaining to ionization potentials (IPs), electron affinities, and monomer separation energies have attracted much attention in the past ten years<sup>1,2</sup>, since they may reflect the electronic shell structure of clusters (the major features of SEPs are associated with steps at magic numbers, but often there is in addition substantial fine structure, such as odd-even alternations).

Due to the required computational effort, first-principles (FP) theoretical studies (which incorporate the ionic geometry) of such SEPs are usually limited to cluster sizes of the order of ten atoms.<sup>3,4</sup> Recently, however, systematic theoretical investigations of such SEPs have been performed for a broad range of cluster sizes using the jellium-related Shell-Correction-Method (SCM) approach.<sup>5-8</sup>

In a recent article, Gardet *et al.*<sup>9</sup> have studied the IPs of small lithium clusters  $\text{Li}_N$  (with  $N \leq 12$ ) using a FP - density functional theory (DFT) and found reasonable agreement between theory and experiment. Furthermore, through a comparison of their results with those obtained from Kohn-Sham local-density-approximation (KS-LDA) calculations on a *spherical* jellium background,<sup>10,11</sup> they concluded that the jellium model is inadequate for a proper description of the IPs of such systems.

The purpose of this comment is to clarify that, while modelling the ions in a cluster via a uniform jellium background is certainly an approximation, the above conclusion of Gardet *et al.* pertains to limitations introduced through neglect of deviations from spherical symmetry, rather than to the jellium approximation itself. Indeed, in a series of papers,<sup>6-8</sup> we have demonstrated that consideration of triaxial shape deformations drastically improves the agreement between the jellium approximation and experiment for all instances of the aforementioned SEPs and for sizes up to 100 atoms, as well as for a variety of metal species (namely, alkali metals, such as Na and K, and noble metals, such as Cu and Ag).

To further elucidate the importance of shape deformations, we display in Fig. 1 the IPs of small  $\text{Li}_N$  clusters (in the same size-range as with Ref. 9) calculated<sup>12</sup> with our SCM for three different families of shapes of the jellium background [namely, spherical, spheroidal (axially symmetric), and ellipsoidal (triaxial)], and compare them to the experimental measurements.<sup>13</sup>

Fig. 1 reveals that spherical shapes (top panel) exhibit a characteristic sawtoothed profile, well known from

previous spherical KS-LDA studies<sup>10</sup> and similar to the curve<sup>14</sup> labeled jellium-LDA in Fig. 12 of Ref. 9. Apart from major-shell closures, this sawtoothed profile describes the data rather poorly (notice in particular the absence of fine structure between major shell closures at  $N = 2, 8$  and  $20$ ).

The spheroidal model (middle panel) exhibits substantial improvement in describing the experimental trend. Furthermore, the ellipsoidal case (bottom panel) improves the agreement between the SCM results and experiment even further, in particular in the size range  $11 \leq N \leq 14$ . The essential improvement introduced by the deformations over the spherical case concerns the very good description of the subshell closure at  $N = 14$  and of odd-even alternations between major shell closures.

In summary, we have illustrated once again that, within the jellium approximation, deformed cluster shapes provide an adequate description of the observed systematic size dependence of the properties of simple metal clusters and should necessarily be employed in comparisons with other theoretical approaches.

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- <sup>11</sup> M.J. Puska, R.M. Nieminen, and M. Manninen, Phys. Rev. B **31**, 3486 (1985).
- <sup>12</sup> In the case of  $\text{Li}_N$  clusters, the parameters entering in the SCM calculation are  $U_0 = -0.035$ ,  $r_s = 3.25$  a.u.,  $t = 2.22$  a.u.,  $\delta_0 = \delta_2 = 0$ ,  $W = 2.31$  eV,  $\alpha_v = -7.985$  eV,  $\alpha_s = 0.629$  eV, and  $\alpha_c = 0.125$  eV (see Ref. 6 for their meaning). The liquid-drop parameters  $\alpha_v$ ,  $\alpha_s$ , and  $\alpha_c$  were specified through a fit to extended-Thomas-Fermi total energy calculations for spherical clusters in conjunction with a *stabilized-jellium*-LDA energy functional [see J.P. Perdew, H.Q. Tran, and E.D. Smith, Phys. Rev. B **42**, 11 627 (1990) and C. Yannouleas and U. Landman, Chem. Phys. Lett. **217**, 175 (1994)]. The need to use the stabilized-jellium-LDA energy functional arises from the fact that the usual jellium-LDA fails to describe the surface energy of metals with high densities (like the case of Li). The mass of the delocalized valence electrons was taken equal to the free-electron mass.
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FIG. 1. IPs for  $\text{Li}_N$  clusters in the range  $2 \leq N \leq 16$ . Solid dots: Theoretical results derived from the SCM (see Refs. 6,7) using three different shape models for the jellium background. Top panel: The spherical model compared to experimental data (open squares). Middle panel: The spheroidal model compared to experimental data. Lower panel: The ellipsoidal model compared to experimental data. The experimental measurements (open squares) were taken from Ref. 13.

